<Division of Materials Chemistry> Chemistry of Polymer Materials

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Prof
FUKUDA, Takeshi
(D Eng)

Assoc Prof
TSUJII, Yoshinobu
(D Eng)

Assist Prof
OHNO, Kohji
(D Eng)

Assist Prof
GOTO, Atsushi
(D Eng)

Students

KOH, Kyoungmoo (D3)
MORINAGA, Takashi (D3)
YOSHIKAWA, Chiaki (D3)
KWAK, Yungwan (D2)
OHKURA, Masahiro (M2)
OMI, Yohei (M2)
INUKAI, Shinich (M1)
OKAYASU, Kenji (M1)
ZUSHI, Hirokazu (M1)
TAKENO, Satoshi (M1)
UEDA, Manabu (UG)
WATANABE, Yuichi (UG)

Visitors

Dr TONGE, Mathew	Stellenbosh University, South Africa, 3 February 2004
Prof MIYATA, Seizo	President, Tokyo University of Agriculture and Engineering, 28 May 2004
Prof WATANABE, Junji	Tokyo Institute of Technology, 28 May 2004
Mr LADMIRAL, Vincent R.	University of Warwick, UK, 6 July - 23 August 2004
Prof HAN, Yanchun	Chinese Academy of Sciences, China, 17 November 2004
Prof MÜLLER, Axel H. E.	Bayreuth University, Germany, 10 December 2004

Scope of Research

Kinetic and mechanistic analyses are made for better understandings of the chemical and physicochemical reactions occurring in polymerization systems and for better routes to the synthesis of well-defined polymers. By various polymerization techniques, in particular, living polymerizations, new well-defined polymers or polymer assemblies are prepared, and their structure/properties relationships are precisely analyzed. Projects in progress include: (1) kinetics and mechanisms of living radical polymerization (LRP). (2) Synthesis of new polymeric materials by living polymerizations and their structure/properties studies. (3) Synthesis, properties, and applications of high-density polymer brushes (HDPB).

Research Activities (Year 2004)

Presentations

Structure and Property of HDPB (Invited Lecture), Tsujii Y, UK-JPN Polymer Workshop 2004, Kyoto, 1 - 2 April.

Precision Design and Application of Organic/Inorganic Hybrid Particles Coated with HDPB (Invited Lecture), Ohno K, and 7 other presentations, 53rd Spring Meeting, Soc. Polym. Sci., Jpn., Kobe, 28 - 30 May.

Structure and Properties of HDPB Formed by LRP (Invited Lecture), Fukuda T, and Rate Retardation in RAFT polymerization, Goto A, and 1 other presentation, 40th World Polymer Congress, France, 4 - 9 July.

Surface Modification by LRP (Invited Lecture), Fukuda T, 51st Summer College, Soc. Polym. Sci., Jpn., Oshima, 12 - 14 July.

4 presentations, 50th Polymer Symposium, Soc. Polym. Sci., Jpn., Kobe, 15 July.

2 presentations, 2nd Trilateral Workshop on Organic Chemistry, Kyoto, 4 - 6 September.

4 presentations, 53rd Autumn Meeting, Soc. Polym. Sci., Jpn., Sapporo, 15 - 17 September.

Structural Studies of HDPB by Neutron Reflectometry (Invited Lecture), Tsujii Y, 4th Annual Meeting of Jpn. Soc. Neutron Sci., Sapporo, 16 - 17 December.

Grants

Fukuda T, Science and Technology of HDPB, Grant-in-Aid for Science Research (A)(2), 1 April 2002 - 31 March 2005.

Tsujii Y, Fundamental Study on HDPB, Grant-in-Aid for Science Research (B)(2), 1 April 2002 - 31 March 2005.

Kinetic Studies on Activation Processes for Organotellurium- and Organostibine-Mediated Living Radical Polymerizations

Organotellurium- and organostibine-mediated LRP (TERP and SBRP, respectively) are new classes of LRP that can provide low-polydispersity polymers in a robust way. The basic concept of LRP is reversible capping of the propagating radical ($P^{\bullet}$) with a capping agent (X) to form a dormant species (P-X), and a prerequisite for achieving low polydispersity is a sufficiently high frequency of activation (decapping of X). In this regard, we determined the activation rate constants for TERP (X = TeMe) and SBRP (X = $SbMe_2$) by the gel permeation chromatography (GPC) method (Figure 1) and established their activation mechanisms. The activation for the TERP of styrene mainly occurred by the degenerative chain transfer (DT) between P-X and $P^{\bullet}$ with a small contribution of the thermal homolysis of P-X. TERP had been believed to be driven by thermal homolysis and thus conducted at high temperatures, but the kinetic result suggested that, with the addition of conventional radical initiator to supply $P^{\bullet}$, TERP can be controlled at lower temperatures with a sufficiently high polymerization rate. This new protocol was confirmed to be effective. The C_{ex} significantly depended on polymers, increasing in the order of methyl methacrylate < styrene < methyl acrylate. For the SBRP of styrene, DT was the only important activation mechanism. The C_{ex} was about twice as large as that for the TERP of styrene, explaining why the SBRP has a better polydispersity controllability than the TERP.

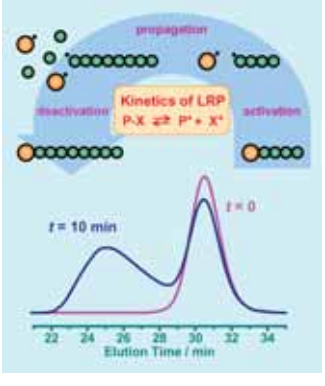

Figure 1. Schematic representation showing the activation, propagation, and deactivation processes in LRP (top) and the evolution of chain length and chain length distribution as followed by GPC (bottom). The activation rate constant was determined by following the decay of the dormant species concentration at the elution count of 30.5 min. This figure is the cover picture of J. Polym. Sci. Part A: Polym. Chem., issue 19, **42** (2004).

Living Radical Polymerization by Polyhedral Oligomeric Silsesquioxane-Holding Initiators: Precision Synthesis of TadpoleShaped Organic/Inorganic Hybrid Polymers

Incompletely condensed polyhedral oligomeric silsesquioxane with the highly reactive group of trisodium silanolate was used for the synthesis of two initiators for atom transfer radical polymerization, one with a 2-bromoisobutyl group (7Ph-T_8-BIE), and the other with a chlorosulfonyl group (7Ph-T_8-CSPE). These initiators were applied to solution polymerizations of styrene and methyl methacrylate (MMA) in the presence of a copper-complex. In both systems, polymerization proceeded in a living fashion, as indicated by the first-order kinetics of monomer consumption, the evolution of molecular weight in direct proportion to monomer conversion, the good agreement of molecular weight with the theoretical one, and the low polydispersity (Figure 2), thus providing tadpole-shaped polymers with an "inorganic head" of polyhedral oligomeric silsesquioxane (POSS) and an "organic tail" of well-defined polymer. Thermogravimetric and differential scanning calorimetric studies showed that both thermal degradation and glass transition temperatures of the organic/inorganic hybrid polymers with molecular weights up to about 20,000 were enhanced as compared to those of model polymers without the POSS moiety.

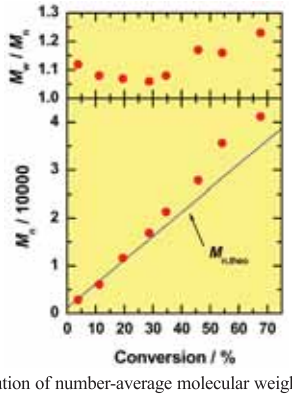

Figure 2. Evolution of number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of POSS-PMMAs as a function of monomer conversion for the solution polymerization of MMA (50 wt %) in anisole at 70°C with 7Ph-T_8-CSPE. The full line in Figure 2 represents the theoretical prediction calculated as the molar ratio of polymerized monomer to the initiator.

Tsujii Y, Nanostructure Control by Mixed Polymer Brushes, Grant-in-Aid for Exploratory Research, 1 April 2003 - 31 March 2005.

Goto A, Chain Length Dependence of kt, Grant-in-Aid for Young Scientists (B), 1 April 2003 - 31 March 2005.

Tanaka K, Construction of Nanoelectronic Devices, CREST, Jpn. Sci. Tech. Corp., 1 November 2002 - 31 October 2007.

Kaya K, Collaboratory on Electron Correlations, Grant-in-Aid for Cre. Sci. Res., 1 April 2001 - 31 March 2006.

Ohno K, Magnetically Tunable Colloidal Crystal, ICR Collaboration, 2004.